

Syntactic Metals: A Survey of Current Technology

Ray Erikson*

Flight Materials Group, 2 Collins Road, Wakefield MA 01880
Tel: 781-246-8239 Email: ray.erikson@flightmaterials.com

Syntactic metals are a relatively new development in materials science. Several approaches to synthesizing these materials have been tried, and the handful of researchers in this field are beginning to make progress in defining useful compositions and processes. Syntactic metals can provide materials with dramatically improved specific strength and stiffness over their parent alloys, while retaining the isotropy that makes ordinary metals preferable to fiber-reinforced laminated composites in many applications. This paper reviews syntactic material concepts in general, the current state of the art (including the author's own work in syntactic aluminum), and the direction of future developments.

Introduction

Syntactic metals are relative newcomers to the world of aerospace materials, and a lot remains to be learned about them. The huge variety of component materials available, the complexities and subtleties of processing, and the tremendous performance potential, have intrigued many investigators. The performance potential stems from the following figures of merit for specific strength and stiffness:

$$\frac{S}{\rho} \text{ and } \frac{E}{\rho} \text{ for strong, stiff tensile members}$$

$$\frac{S^{2/3}}{\rho} \text{ and } \frac{E^{1/2}}{\rho} \text{ for beams, shafts, columns}$$

$$\frac{S^{1/2}}{\rho} \text{ and } \frac{E^{1/3}}{\rho} \text{ for plates and shells}$$

where S is strength, E is modulus, and ρ is mass density. The specific strength and stiffness of a structure goes up much more quickly with decreasing density than with increasing strength or modulus — that is why we build more flight vehicles from aluminum than steel.

The earliest work in this area was presented in 1984 by Keshavaram et al at a conference in India. He and his colleagues investigated the behavior of some flyash- and glass-microsphere reinforced aluminum composites [13].

In 1989, Rickles, working under Cochran at the Georgia Institute of Technology, used hollow aluminum oxide spheres in his Master's Thesis on their experiments with what they called "Metal/Ceramic Syntactic Foam" [27]. Cochran has since focused on producing metallic spheres of nickel, titanium and stainless steel sintered together to form ultralight ($\rho < 1.0 \text{ g/cm}^3$) all-metal syntactic foams with no matrix material [5, 6].

A team led by Rawal at Lockheed Martin Astronautics in Denver, Colorado, investigated what they also called "syntactic metal foams." From the late 1980's to the mid 1990's they produced several experimental material systems using hollow aluminum oxide spheres in A201 and A356 aluminum, and in Ti6Al4V titanium matrices [22, 23, 24, 25].

Using a pressure casting system very similar to the one developed by Blucher at Northeastern [4], Rawal made sandwich panels

*Principal Engineer. Copyright©2002 by author.

with titanium facesheets and Hollow Ceramic Microsphere/Aluminum (HCM/Al) composite cores, where the titanium provided the preform in the pressure casting process. They also made some stand-alone plates of HCM/Ti composite, and investigated the reactions at the interface between the aluminum oxide spheres and the titanium matrix.

Rawal and his colleagues noted that as the mean microsphere diameter was decreased from 2300 microns to 60 microns the compressive strength of their A201 matrix composite increased from 30 to 65 ksi. Because the smaller spheres had proportionately thicker shells, the density also increased from 1.96 to 2.90 g/cc, but this still resulted in a net increase in specific strength over the parent alloy.

In 1993, Rohatgi patented a slurry method of forming metal matrix composites using flyash (mixed silica, alumina, iron and titanium oxides), glass or ceramic microspheres [26].

In 1996, Kampe of Virginia Tech conducted investigations of flyash-reinforced aluminum and titanium in association with University Partners, Inc. and Oak Ridge National Laboratory [12]. Additional studies of flyash composites have been made by investigators in Australia and India [18, 30, 13, 28, 29].

Since 1995, researchers at the University of California at Santa Barbara have used aluminum oxide spheres with A201 and A360 aluminum matrices in a series of detailed studies correlating measured properties with those predicted by a finite element model [14, 15]. This work has used relatively large spheres with mean diameters of 1.0, 1.5 and 2.5 mm, with corresponding relative wall thickness aspect ratios (t/R) of 0.5, 0.3 and 0.1, respectively.

The finite element models used by the UCSB researchers predicted significant increases in both strength and modulus compared to the unmodified matrix materials. Experimental results have been mixed; while some syntactic samples have displayed higher moduli and yield strengths up to three times as high as the corresponding neat alloy, other samples

have failed at lower relative values. This has been attributed to residual thermal stresses developed in the spheres themselves during cooling, resulting in sphere cracking, especially in the larger, thinner spheres.

In 1998 and 1999 at Northeastern, Blucher and the author, using experience gained with polymer-matrix syntactics on a military aircraft program, began a study of aluminum matrix syntactics [7, 8]. Hollow alumina, mullite, glass and flyash microspheres ranging in size from 10 to 3000 microns were used in 413 (eutectic Al-Si), 1100, 2024 and pure aluminum.

The same phenomena as that described by the UCSB researchers were observed with larger (> 1000 micron) alumina spheres, but significantly different behavior was seen in smaller spheres of different compositions. The smaller spheres (< 200 micron) were much more stable against local failure, even with aspect ratios comparable to the larger spheres.

This work confirmed what had been observed by earlier workers in flyash; i.e., that reactions between the microspheres and the matrix, regarded as a nuisance by some researchers, appear to induce very useful bonding mechanisms for maintaining the integrity of the composite under loading.

In 1999, Cochran, Sanders, Nadler and others [20] began working with nickel and steel spheres in aluminum matrices — an approach that can obviously be extended to all sorts of useful alloy combinations.

Around that same time, PowderMet in Sun Valley, California, began developing metallic syntactics for aerospace applications by coating ceramic spheres with metals and sintering them together to produce materials with a wide variety of compositions and densities.

Composition

Alloys used so far in syntactic metals include pure aluminum, nickel and titanium; 201, 356, 360, 413, 1100, 2024 and 6061 aluminum; 405

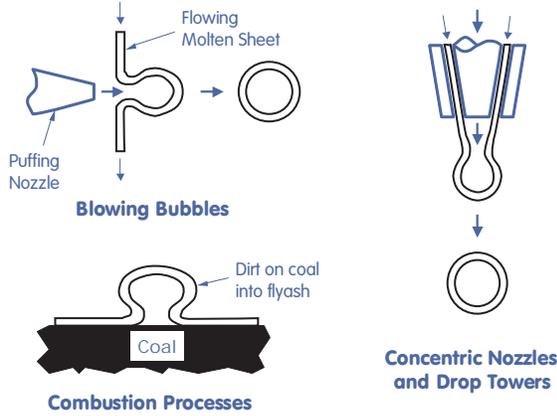


Figure 1: Methods of producing microspheres.

stainless steel and 6-4 titanium. PowderMet is also experimenting with molybdenum and rhenium alloys.

Microspheres can have many different compositions and are produced by several different methods, which include (1) using a puffing nozzle to blow bubbles from a flowing molten sheet of material; (2) using a concentric nozzle and a drop tower; (3) using the flyash produced by contaminants on coal; and (4) sol-gel methods. The first three are shown in Figure 1.

The microspheres investigated by the author in his own work encompass most of the spheres used by others. These include mullite spheres from Keith Ceramics in England; 14/40 and 36/F “Duralum AB” alumina spheres from Washington Mills in North Grafton, Massachusetts; “Aerospheres” (alumina) from Georgia Institute of Technology in Atlanta, Georgia; LV01, TV09 and AP05 “Recyclospheres” (flyash) from Sphere Services in Oak Ridge, Tennessee; SLG and SL-150 “Extendospheres” (flyash) from PQ Corporation and 110P8 “Sphericels” (borosilicate glass) from Potters Industries, both in Valley Forge, PA.

Sphere Price and Availability

Over fifty manufacturers of microspheres and ceramic products were contacted to define the price and availability of hollow ceramic microspheres. Price ranged from \$1.50/lb for

flyash-derived spheres to \$4.00/lb for glass spheres to “very expensive” for the pure aluminum oxide spheres from Georgia Tech. Flyash and glass spheres are readily available; other types have lead times of weeks to months. Key findings:

- The smallest hollow ceramic microspheres currently available are 3M G-200 “Zeeospheres” with a mean diameter of 4.4 microns; however, with a density of 2.5 g/cc, they are not the best candidates for composites of aluminum and titanium. The smallest hollow microspheres with a true density under 1.0 g/cc are the Potters Industries 110P8 Sphericels with a mean diameter of 10 microns.
- There are currently only two sources of pure aluminum oxide hollow microspheres: Washington Mills and Georgia Tech. The Washington Mills spheres are small ($\sim 100 \mu\text{m}$), cheap (\$1.00/lb) and readily available, but very rough and very porous, requiring a good deal of preprocessing, such as buoyant separation, before use. The Georgia Tech spheres are of excellent quality for composite use.

Sphere Density

Density measurement is a critical part of the production of lightweight materials. Measuring the density of microspheres is not as simple as it might seem, since in bulk the material behaves like neither solid nor liquid, but somewhere in between.

Bulk and tap density are readily determined with a graduated cylinder and a scale, although special standardized density testers (that apply standard tapping to the cylinder) have, of course, been developed. The true particle density of the spheres is more challenging. Devices called *pycnometers* have been developed to automate the process using liquids or gases to provide displacement information. Table 1 compares experimental values obtained by the author with vendor data sheet values.

Table 1: Experimental densities (g/cc) versus supplier specifications.

Supplier	Grade	Spec.	Meas.
PQ Corp.	SLG	Bulk	0.40
		True	0.41
Washington Mills	4/10	Bulk	0.60
		True	0.48
	10/20	Bulk	0.65
		True	0.89
Sphere Services	AP05	Bulk	0.37
		True	0.32
	TV09	Bulk	0.64
		True	0.51
		Bulk	0.36
		True	0.33
		Bulk	0.54
		True	0.52

True density can be used to complete morphological studies. While much information can be gathered by studying the exterior of the spheres with a microscope, direct determination of shell thickness depends upon observation of fractured spheres. With true density information, the mean shell thickness may be estimated from a relation developed by the author in previous work [7] as follows:

$$t = \frac{d}{2} \left\{ 1 - \left[1 - \left(\frac{\rho_t}{\rho_s} \right) \left(\frac{6a^3}{\pi N_u} \right) \right]^{1/3} \right\} \quad (1)$$

where d is the mean diameter, ρ_t is the true density, ρ_s is the shell material density, a is an empirical constant related to sphere packing efficiency with a typical value around 1.07, and N_u is another empirical constant with a typical value around 1.45. The shell thickness may then be used to calculate the sphere strength, though the details of that process are far beyond the scope of this paper.

Table 2: Composition of typical flyash-derived ceramic microballoons (%).

Component	PQ-SLG	SS-AP05	SS-TV09
SiO ₂	59.0	60.0	54.5
Al ₂ O ₃	38.0	31.8	36.1
Fe ₂ O ₃	0.5	4.3	5.6
TiO ₂	1.7	1.3	1.3
Other	0.8	2.6	2.5

Chemistry

Chemical analysis can be performed using acids to dissolve the spheres so that they may be treated with reagents in solution using “wet” chemistry methods. Alternatively, the spheres may be ground into fine powders and atomized into plasma streams for atomic emission (AE) spectroscopy. For microspheres that contain silicon, these techniques can be unreliable, because of secondary reactions that occur during processing.

The most reliable chemical analysis methods for powdered substances are x-ray diffraction, x-ray spectroscopy, auger electron spectroscopy, x-ray photoelectron spectroscopy, and ion-scattering spectroscopy [16]. Vendor specifications for PQ and Sphere Services products are listed in Table 2.

Processes

Processing Microspheres

Given a source of stock microspheres, it may still be necessary to separate spheres from a given batch by size, weight, and/or porosity. Several methods of separating desired spheres from undesired spheres were investigated during the course of this research.

Screening is a familiar process: increasingly fine wire meshes sort small particles from big

ones. Standard sieve sizes were first established in 1910. In 1970 the American Society for Testing Materials (ASTM) joined with the International Standards Organization (ISO) to define international sieve standards ASTM E11 and ISO 565. Although straightforward, conventional screening is limited to about the 400 mesh level (37 microns). At that size, the bulk powder has the consistency of baking flour. Finer particle resolution requires use of fluid filtering techniques, but even these become ineffective for particle sizes below about one micron.

Some commercial separators use a combination of mechanically-induced vibration screening and airflow. These are known as gravity separators, which are widely used in the agriculture and food processing industries for separating seeds and grains.

The author has used buoyant separation to obtain useful microspheres from raw stock. In any given batch of commercial microspheres, many will be broken or have wall thicknesses that make them nearly solid. Buoyant separation can be effective at eliminating both broken and excessively thick microspheres from a batch. The biggest obstacle to its use is microsphere density, since even relatively light spheres can have a true density approaching that of water. A variety of liquids were subjected to experiment.

Since the sphere shell material will be heavier than any common liquid, broken spheres and loose shards should, in theory, sink to the bottom. In practice, surface tension can skew the results. Spheres with small holes or cracks may float because the liquid surface tension prevents flow into the sphere. The smaller the sphere size, the greater the impact of surface tension. This problem can be ameliorated to some extent by the addition of surfactants.

Making Composites

The combination of spheres and matrix materials has been one of the main impediments to progress in this field. Blucher, Rawal and the author have used pressure infiltration. This

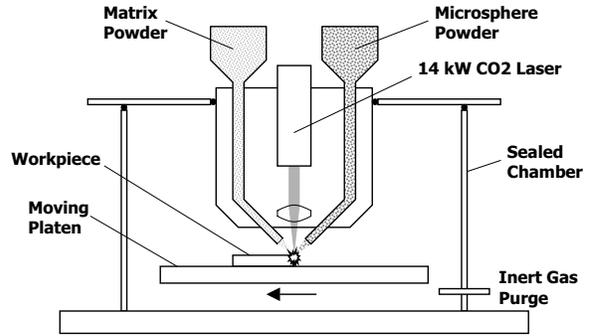


Figure 2: Direct laser sintering approach to syntactic metal development.

method is tried and true in the laboratory fabrication of metal matrix composites, but it is not a method that lends itself to widespread commercial application.

Slurry mixing makes use of the fact that the viscosity of a fluid increases with the addition of small particles. Some researchers have found that simply mixing the microspheres into a melt increases the viscosity of the melt enough to get a reasonably uniform sphere distribution.

Conventional powder metallurgy methods involving compaction for sintering have also been tried, but the fragility of individual hollow ceramic spheres does not lend itself to these processes readily. PowderMet has sidestepped the problem by coating the spheres with metal first, then sintering the *coatings* together.

Some new methods of fabrication may be derived from rapid prototyping techniques, such as Selective Laser Sintering (SLS) by DTM/3D Systems; RapidSteel from DTM Corporation; or LasForm by AeroMet. A notional diagram of this approach is shown in Figure 2.

Structure

Microsphere Structure

General particle structure can be determined with a low magnification light microscope or a scanning electron microscope (SEM). Several microsphere types have been examined by

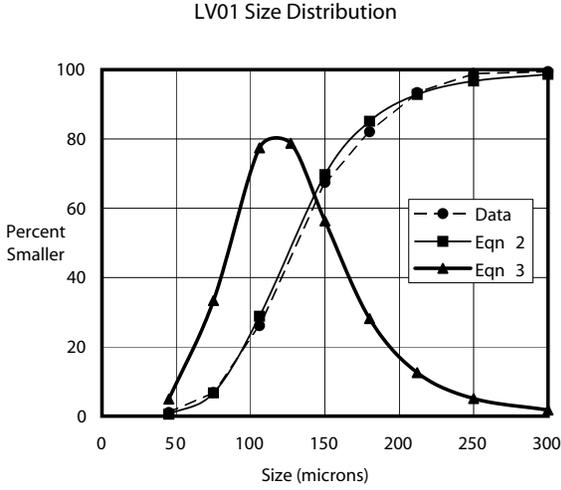


Figure 3: Size distribution curves for Sphere Services TV09 microballoons.

the author under both optical and electron microscopes. In shape, all microspheres examined are reasonably spheroidal. Surface texture ranges from relatively rough and irregular on the Washington Mills spheres to glassy on the PQ Sphere Services products. The Washington Mills aluminum oxide spheres and the mullite spheres from Keith Ceramics were also much more porous than the others.

Size and size distribution may be determined from vendor data, image analysis or screening. Distributions for one of the Sphere Services products, based on particles retained in a standard sieve series, are shown in Figure 3, where a cumulative distribution function has been fitted using the sigmoidal relation

$$F(x) = 100 - \frac{100}{1 + \left(\frac{x}{x_F}\right)^H} \quad (2)$$

where x is a particle size, x_F is the estimated mean particle size, and H is a curve shape factor. Given the cumulative distribution, the frequency distribution may be found from

$$f(x) = \frac{dF}{dx} = \frac{8000 \left(\frac{H}{x_F}\right) \left(\frac{x}{x_F}\right)^{H-1}}{1 + 2 \left(\frac{x}{x_F}\right)^H + \left(\frac{x}{x_F}\right)^{2H}} \quad (3)$$

Size distribution may also be determined by screening, sedimentation, light scattering methods, electrozone size analysis, optical sensing zone analysis, and Fisher sub-sieve size analysis. All of these techniques have been commercialized into off-the-shelf lab equipment for batch analysis.

Composite Structure

A syntactic metal may be two-phase or three-phase. Two-phase syntactics can consist of metal or ceramic microspheres and the matrix metal (see Figure 4); or they can be comprised of metal microspheres sintered together, and the space between them. Three-phase syntactics consist of ceramic microspheres, metal coatings and the menisci they form, and the space between them.

A single sphere size can produce a density reduction of about 50 percent in a fully-infiltrated two-phase syntactic. By using multimodal size distributions to fill the interstices, density can theoretically be reduced to any desired level, though 20 percent that of the parent alloy is probably the near-term practical limit.

For producing a smooth skin on finished parts to improve strength and endurance, facesheets may be applied to form a conventional sandwich. On more complex geometries, various deposition techniques such as electroforming, flame spraying, etc. may be employed to form a “3-D sandwich.”

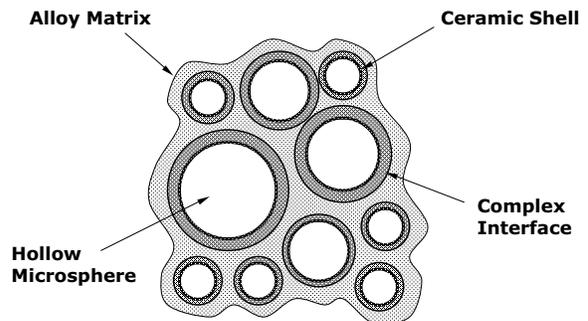


Figure 4: Cross-section of fully-infiltrated two-phase syntactic.

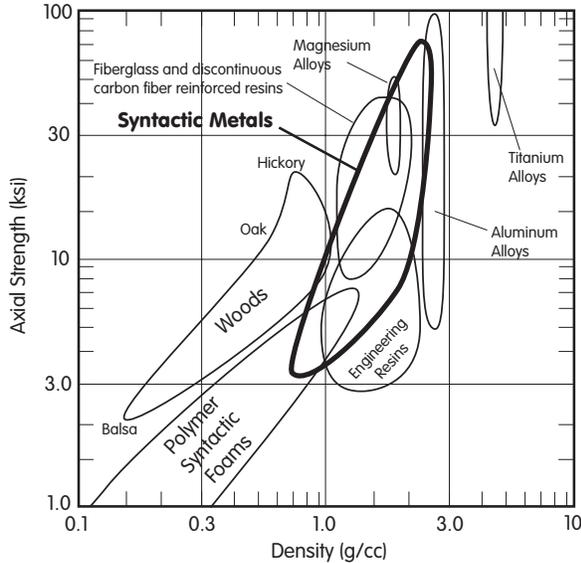


Figure 5: Ashby diagram showing ranges of strength and density achieved to-date in syntactic metals.

Properties

As with any composite, each property of a syntactic metal follows some form of mixture rule, though these rules tend to be somewhat more complicated than the usual partition by volume fraction. This is due to the tremendous range of interaction possible between the spheres and the matrix in denser systems, and the micro-mechanical behavior of the spheres themselves in lighter systems. The ranges of strength and density achieved by various workers so far are outlined in the Ashby diagram of Figure 5.

Modulus tends to decrease with decreasing density, but not necessarily linearly. The author has measured a modulus of 7.0 Msi in syntactic aluminum with a density of 1.69 g/cc, and it should be possible to tune composite modulus to some extent by appropriate selection of microsphere characteristics and volume fraction.

Other properties, such as thermal strain rate and thermal conductivity have yet to be investigated fully, but the combination of ceramic and metals suggests they may have excellent stability for cryogenic optics. Refractory alloys such as molybdenum and rhenium become

more appealing for propulsion and electronics applications at lower densities. Syntactic metals may also provide a path to improved radiation shielding.

Although specific strength improves simply by reducing density, more may be possible by using the microspheres for dispersion hardening. Second phase hardening is derived from the line-tension model as

$$\frac{F}{L} = \frac{T}{R} = \frac{\alpha G b^2}{R} \quad (4)$$

where F is the force on an individual obstacle (particle), L is the distance between particles, T is the line tension in the dislocation encountering the obstacles, R is the radius of the bow produced in the dislocation, α is a constant (≈ 1), G is the shear modulus, and b is the Burgers vector. Orowan and Ashby have described this effect in terms of shear stress as

$$\tau_{sp} = \frac{0.8Gb}{2\pi L\sqrt{1-\nu}} \ln\left(\frac{2r}{r_o}\right) \quad (5)$$

where r is the size of the particle and r_o is the inner cutoff radius ($\approx b = a/2$, where a is the lattice constant). The Orowan-Ashby relation suggests that with small enough hollow microspheres (on the order of Buckyballs), syntactic metals could be up to three times as strong, as well as half as heavy, as current alloys.

Even with only modest reductions in microsphere size, other strengthening effects can make themselves apparent. For instance, Unsworth and Bandyopadhyay [34] explored the effect of 10–100 μm solid microspheres on dislocation and precipitate formation in the parent alloy. A mean strength gain of 31% was obtained in these composites relative to conventional 6061-T6 aluminum. They theorized that the observed strength increase was due to the following set of phenomena:

- Since ceramic microspheres have much smaller thermal strain rates than the aluminum, significant residual stresses develop in the matrix during cooling.
- These residual stresses increase the dislocation density in the matrix.

- The increased dislocation density facilitates the formation of larger numbers of Guinier-Preston zones and precipitates during subsequent heat treatment.
- The additional G-P zones and precipitates provide additional obstacles to dislocation motion during deformation.

Rawal and his colleagues also noted that as the mean microsphere diameter was decreased from 2300 microns to 60 microns the compressive strength of their A201 matrix composite increased from 30 to 65 ksi; i.e., more than doubled. Because the smaller spheres had proportionately thicker shells, the material density also increased from 1.96 to 2.90 g/cc, but a net increase in specific strength over the virgin A201 was still achieved.

Conclusions

Syntactic metals are a new class of metal matrix composites. They can achieve better specific strength and stiffness in particular applications than current alloys simply by lowering material densities. They have the same potential for increased absolute strength as dispersion-strengthened alloys. With sufficient development of component materials and synthesis processes, syntactic approaches should be able to make light alloys significantly lighter, and heavier alloys more palatable, in flight structural, propulsion, optical, thermal control and shielding applications.

References

- [1] Ashby, M.F. (1999). *Materials Selection in Mechanical Design, 2nd Edition*. Boston: Butterworth-Heinemann.
- [2] Ashby, M.F. et al. (2000). *Metal Foams: A Design Guide*. Boston: Butterworth-Heinemann.
- [3] Bardella, L. & G. Francesco. (2001). On the elastic behavior of syntactic foams. *International Journal of Solids and Structures*, Vol.38, 7235–7260.
- [4] Blucher, J.T. (1992). Liquid metal pressure infiltration to produce metal matrix composites. *Journal of Materials Processing Technology*, 30, 381–390.
- [5] Clancy, R.B., Cochran, J.K. & Sanders, T.H. (1995). Fabrication and Properties of Hollow Sphere Nickel Foams. In D.L.Wilcox et al (Eds.), *Hollow and Solid Spheres and Microspheres: Science and Technology Associated With Their Fabrication and Application, MRS Symposium Proceedings, Volume 372*. Pittsburgh: Materials Research Society, 155–163.
- [6] Clancy, R.B., Sanders, T.H. & Cochran, J.K. (1991). Fabrication of Thin-Wall Hollow Nickel Spheres and Low Density Syntactic Foams. In E.W.Lee & N.J.Kim (Eds.), *Light-Weight Alloys for Aerospace Applications II*. Pittsburgh: The Minerals, Metals & Materials Society, 477–485.
- [7] Erikson, R.J. (1996). Mechanical evaluation of ARC syntactic foams. Nashua NH: Lockheed Martin report P950101-9.
- [8] Erikson, R.J. (1999). Syntactic aluminum: Hollow ceramic microsphere reinforced metal matrix composites (Master’s Thesis). Boston: Northeastern University.
- [9] German, R.M. (1994). *Powder Metallurgy Science, 2nd Edition*. Princeton NJ: Metal Powder Industries Federation.
- [10] Gibson, L.J. & Ashby, M.F. (1997). *Cellular Solids, Structure and Properties, 2nd Edition*. New York: Cambridge Univ. Press.
- [11] Charles Hendricks. (1986). Method for Producing Solid or Hollow Spherical Particles of Chosen Chemical Composition and Uniform Size. U.S. Patent 4,774,037.
- [12] Kampe, S.L. (1996). Composites of metal reinforced by flyash. Virginia Tech VTIP 96.041.

- [13] Keshavaram, B. N.; Satyanarayana, K. G.; Majumdar, B.; Rohatgi, P. K.; Dattaguru, B. (1984). Studies on fracture and strength behaviour of Al-glass and Al-flyash particulate composites. *Fracture 84: Proceedings of the 6th International Conference on Fracture (ICF6)*, New Delhi, India. Vol. 4, pp2979–2987. Published by Pergamon Press, New York.
- [14] Kiser, M.T., He, M., Wu, B. & Zok, F.W. (1995). Compressive Deformation of Hollow Microsphere Reinforced Metal Matrix Composites. In D.L.Wilcox et al (Eds.), *Hollow and Solid Spheres and Microspheres: Science and Technology Associated With Their Fabrication and Application, MRS Symposium Proceedings, Volume 372*. Pittsburgh PA: Materials Research Society, 173–178.
- [15] Kiser, M.T., M. He, & F.W. Zok. (1999). Mechanical response of ceramic microballoon reinforced aluminum matrix composites under compressive loading. *Acta Metallurgica* Vol.47, No.9, 2685–2694.
- [16] Klar, E. (Ed.). (1984). *Metals Handbook Volume 7: Powder Metallurgy*. Metals Park OH: American Society for Metals.
- [17] Libenson, G. A. ; Lopatin, V. Y. (2001). Investigation of syntactic foam-type porous powder materials. *Conference: PM2TEC 2001: 2001 International Conference on Powder Metallurgy & Particulate Materials, New Orleans, 13–17 May 2001*.
- [18] Liu, X.; Nilmani, M. (1996). The effect of particle volume fraction on the mechanical properties of aluminum flyash MMC. *Proceedings of Processing, Properties, and Applications of Cast Metal Matrix Composites, Cincinnati, 7-9 Oct. 1996*. Publisher: Minerals, Metals and Materials Society; Warrendale PA.
- [19] Murray, J.L. & McAlister, A.J. (1984). The Al-Si (Aluminum-Silicon) System. *Bulletin of Alloy Phase Diagrams*, 5(1), 74–84.
- [20] Nadler, J. H. ; Hurysz, K. M. ; Clark, J. L. ; Cochran, J. K. ; Lee, K. J. ; Sanders, T. H. (1999). Fabrication and microstructure of metal-metal syntactic foams. *Conference: MetFoam 99: International Conference on Metal Foams and Porous Metal Structures, Bremen, Germany, 14–16 June 1999*. pp179–182.
- [21] Petzow, G. & Effenberg, G. (1990). *Ternary Alloys, Volume 3: Al-Ar-O to Al-Ca-Zn*. Weinheim, Germany: VCH.
- [22] Rawal, S.P. & Misra, M.S. (1989). Development of a Ceramic Microballoon Reinforced Metal Matrix Composite. In 34th SAMPE Symposium on *Tomorrow's Materials: Today*, 122–125.
- [23] Lanning, B.R., Rawal, S.P. & Misra, M.S. (1989). Interface Structure of a Cast Alumina Microballoon Reinforced Titanium Composite. In Gungor, Lavernia & Fishman (Eds.), *Proceedings of the Advanced Metal Matrix Composites for Elevated Temperature Conference*, 79–84.
- [24] Rawal, S.P., Lanning, B.R. & Misra, M.S. (1992). Effect of Reinforcement Size and Distribution on Mechanical Properties of Microballoon Reinforced Metal Matrix Composites. Presented at *Aeromat '92*, Anaheim CA.
- [25] Rawal, S.P., Lanning, B.R. & Misra, M.S. (1995). Processing and Mechanical Properties of Ti/(Alumina)mb/Al Core//Ti Sandwich Panels. In D.L.Wilcox et al (Eds.), *Hollow and Solid Spheres and Microspheres: Science and Technology Associated With Their Fabrication and Application, MRS Symposium Proceedings, Volume 372*. Pittsburgh PA: Materials Research Society, 269–275.
- [26] Rohatgi, P. K. (1993). *Synthesis of Metal Matrix Composites Containing Flyash, Graphite, Glass, Ceramics or Other Metals*. U.S. Patent 5,228,494.

- [27] Rickles, S.A. (1989). Microstructural and Compressive Properties of a Metal/ Ceramic Syntactic Foam. (M.S. Thesis). Atlanta: Georgia Institute of Technology.
- [28] Satapathy, L.N. (2000). A study on the mechanical, abrasion and microstructural properties of zirconia-flyash material. *Ceramics International*, Vol. 26 (1), 39–45.
- [29] Satapathy, L.N. (1998). The physical, thermal and phase identification studies of zirconia-flyash material. *Ceramics International*, Vol. 24 (3), 199–203.
- [30] Sharma, S.C. et al. (1989). Fabrication and testing of flyash dispersed Al–Zn–Mg–Cu high strength particulate composites. *Proc. Seminar on Science and Technology of Composites, Adhesives and Sealants , Bangalore, India, 28–30 Sep 1989*.
- [31] Sinha, S.H. & Rao, G.N. (1976). Cellular Metal. *NML Technical Journal*, 18, 21–24.
- [32] Torobin, L.B. (1981). Method and Apparatus for Producing Hollow Metal Microspheres. U.S.Patent 4,415,512.
- [33] Torobin, L.B. (1990). Method for Producing Hollow Microspheres Made From Particle Compositions. U.S. Patent 5,225,123.
- [34] Unsworth, J.P. & Bandyopadhyay, S. (1994). Effect of Thermal Aging on Hardness, Tensile and Impact Properties of an Alumina Microsphere-Reinforced Aluminum Metal Matrix Composite. *Journal of Materials Science*, 29, 4645–4650.
- [35] Wilcox, D., Liu J. & Look. (1994). Hollow Ceramic Microspheres by Sol-Gel Dehydration With Improved Control Over Size and Morphology. U.S. Patent 5,492,870.
- [36] Liu, J. & David Wilcox. (1995). Factors Influencing the Formation of Hollow Ceramic Microspheres. *Journal of Materials Research*, 10, 84–94.